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The Calculation of Coefficients of Coulomb and Exchange Integrals in Matrix Elements Involving Polar Singlet Structures

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Starting from Pauling's rules for calculating matrix elements for covalent structures, it is shown how to extend the valence-bond treatment to polar structures. Attention is called to the new types of integrals which are involved and simple procedures for evaluating their coefficients are described.

THE valence-bond method for calculating molecular energy levels, first used by Heitler and London,[1] has been developed by Slater[2] and Pauling[3] for the case of singlet states in such a way as to be easily applicable to complex molecules.[4]

One of the most important criticisms of this usual valence-bond method is that the requirement of one and only one electron per orbital overemphasizes the electron-electron repulsions. It has often been stated that this deficiency could be avoided by the introduction of polar structures; however, we have found in the literature only one attempt, by Sklar,[5] to include them in an actual calculation for a complex molecule. It is not quite clear how Sklar's calculation was carried out; and, furthermore, the ionic resonance energy for an isolated double bond, the value of the single exchange integral, and the heat of hydrogenation of a pure covalent double bond were evaluated by methods which seem inappropriate. Very recently, Craig[6] has worked out the same problem but with consideration only of structures with the charges on adjacent atoms; the differences between his and our assumptions and results will be pointed out in a later paper.

THE SLATER-PAULING TREATMENT

The Slater-Pauling treatment makes use of a completely antisymmetrized product type of wave function, which for a system involving N electrons 1, 2, $\cdots$ and N specific spin-orbit functions A, B, $\cdots$, is

$$\psi=\frac{1}{(N!)^{\frac{1}{2}}}\sum_P(-1)^P PA(1)B(2)\cdots E(N). \quad (1)$$

In general, there are more than N suitable spin-orbit functions; and it is necessary to take into account the corresponding degeneracy, which can often be separated into spin degeneracy and orbital degeneracy. In case of orbital degeneracy more than one ψ, involving different combinations of orbitals, has to be considered. Orbital degeneracy occurs, for example, when there are more available atomic orbitals than electrons. There is always spin degeneracy, and it is necessary to consider all possible distributions of spin which give the desired (singlet) multiplicity. To every conventional valence-bond structure there can be assigned a combination of functions which represents a singlet state. Not all such functions are independent but they do form a complete set: Rumer[7] found that, if the orbitals are arranged in a ring and connected in pairs by nonintersecting straight lines in all possible ways, the corresponding functions form a complete, mutually independent set. These sets were called canonical by Pauling.

In order to specify the sign of the function associated with a bond diagram, it is necessary to write each bond as a vector: $a\rightarrow b$, $c\rightarrow d$, $\cdots$ then corresponds to the wave function,

$$\psi=\frac{1}{2^{n/2}}\sum_R(-1)^R R\left\{\frac{1}{(2n)!^{\frac{1}{2}}}\sum_P(-1)^P \times Pa(1)\beta(1)b(2)\alpha(2)c(3)\beta(3)d(4)\alpha(4)\cdots\right\}, \quad (2)$$

where n is the number of bonds, β and α are the two spin functions, and a, b, etc., the atomic orbital functions—so that $a\beta$ is an example of the spin-orbit functions A, B, etc., indicated in Eq. (1); P represents the $(2n!)$ permutations of the orbits and their associated spins among the electrons 1, 2, $\cdots$, $2n$; and R represents the 2^n interchanges of β and α for orbits bonded together. The factor $(-1)^R$ is equal to $+1$ for an even number of interchanges and -1 for an odd number, and $(-1)^P$ is equal to $+1$ or -1 according to whether P is an even or an odd permutation. For canonical structures the convention is adopted of initially assigning the spin function β and the tail of the arrow to orbital a, α and the arrow head to b, and so on. Then, if only spin degeneracy is involved, and only coulomb and single-exchange integrals are retained, Pauling's superposition diagrams (the arrowheads are no longer needed to define the signs) make it possible to build up the secular equation very quickly. For structures X and Y the

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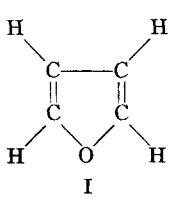
† Contribution No. 1495
[1] W. Heitler and F. London, Z. Physik 44, 455 (1927)
[2] J. C. Slater, Phys. Rev. **38**, 1109 (1931).
[3] L Pauling, J. Chem. Phys. **1**, 280 (1933)
[4] L Pauling and G. W. Wheland, J. Chem. Phys **1**, 362 (1933); L Pauling and J. Sherman, *ibid.*, **1**, 679 (1933).
[5] A. L. Sklar, J. Chem. Phys. **5**, 669 (1937).
[6] D P Craig, Proc Roy Soc. (London) **200**, 390 (1950).
[7] G. Rumer, Nachr. Ges. Wiss. Gottingen, Math-physik Klasse, p 337 (1932); G Rumer, E. Teller, H. Weyl, *ibid*, p 499 (1932).

coefficient of the coulomb integral in the matrix element H_{XY} of the hamiltonian is given by $K=\frac{1}{2}^{n-i}$ and of the single-exchange integrals by $K'=f/2^{n-i}$, where n is the number of orbitals and i the number of islands in the superposition patterns; f is a coefficient that is equal to 1 if the two exchanged orbitals are in the same island and separated by an odd number of bonds, to -2 if they are in the same island and separated by an even number of bonds, and to $-\frac{1}{2}$ if they are in different islands. A customary further simplifying assumption is that all single exchange integrals between nonadjacent atoms are disregarded (the expression "adjacent atoms" refers to the true molecule and not to the arbitrary diagrams of cannonical structures or superposition patterns). Similarly, in the evaluation of the orthogonality integral Δ_{XY}, i.e., the matrix element of unity, all terms corresponding to any exchange integral in H_{XY} are usually neglected, while the term corresponding to the coulomb integral is taken equal to 1, so that Δ_{XY} is equal to K.

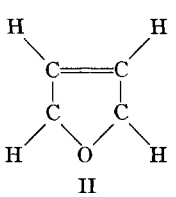
INCLUSION OF POLAR FORMS

The inclusion of polar terms in the valence-bond method ought to be useful for many purposes: to obtain a better value for the principal resonance integral α; to find a better distribution of charge, thus making it possible to calculate electric moments for polar molecules; to treat ions and the molecules of heterocyclic compounds such as pyridine, pyrrole, furan, etc; and to discuss electronic spectra.

Heretofore, the valence-bond method has been applied mainly to unsaturated hydrocarbons and their radicals; it would seem that the nearly constant value found for the exchange integral α means simply that the ratio of resonance energy from covalent structures to that from polar structures is not far from constant in such molecules. But for heterocyclic compounds this cannot be true; for example, as was pointed out by Wheland,[8] furan has a much bigger resonance energy than cyclopentadiene, just because furan, in addition to structures I and II

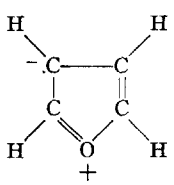


I

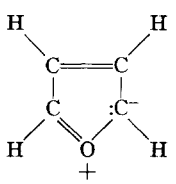


II

involves ionic structures such as III and IV



III



IV

[8] G. W Wheland, *The Theory of Resonance* (John Wiley and Sons, Inc , New York, 1944), p. 62.

which may be expected to be much more important than are their counterparts for cyclopentadiene.

When polar forms are considered the first thing is to see which of all possible polar structures have to be added to the purely covalent structures to get a complete set of mutually independent singlet structures. It appears that in analogy to Rumer's theorem a complete set of structures is obtained on arranging the electrons in the available atomic orbitals in all different ways, singly or in pairs, and for each of these ways forming the canonical bond structures for the single electrons. The corresponding wave functions are given by Eq. (2) with three changes: (1) a particular orbital may appear, naturally, not only once but twice or not at all, and if it appears twice, must be associated once with spin α and once with spin β; (2) the required set of spin-orbit permutations P and spin reversals R may be achieved either by allowing all permutations of spin-orbits among the electrons and spin reversals for bonded pairs only, or by omitting those permutations which involve exchange of spin-orbits having the same orbital parts while permitting spin reversal for these pairs just as for the bonded pairs; and (3) the normalization factor becomes

$$[2^c\cdot(2n)!]^{-\frac{1}{2}}=[2^n\cdot 2^{-p}(2n)!]^{-\frac{1}{2}},$$

c, p, and $2n$ being the numbers of covalent bonds, unshared pairs, and total electrons, respectively.

When polar structures are considered, the matrix elements of $\mathbf{H}$ involve new classes of integrals besides the familiar coulomb and exchange integrals Q and α. Among these are coulomb integrals Q' for the polar structures, exchange integrals γ and γ' corresponding to an atom-atom jump by just one electron, where we call the integral γ for one covalent and one polar structure and γ' for two polar structures, and exchange integrals α' involving one or two polar structures and two electron jumps. If in this case both electrons jump from one atom to an adjacent atom, however, the integral is of the form of α and, indeed, is exactly equal to α if the two orbitals are identical. Of course, not all integrals of a class will have the same value; but we shall not discuss their differences here. Neither shall we further consider exchange integrals involving electron jumps between nonadjacent atoms or jumps of more than two electrons.

CALCULATION OF MATRIX ELEMENTS

In order to approach the problem of evaluating the coefficients of these integrals in the matrix elements we may first consider a two-electron case involving three structures,

$$\begin{array}{ccccccc} 1\ 2 & & 12 & & & & 12 \\ A\text{—}B, & & A: & B, & \text{and} & & A\ B: \\ \text{I} & & \text{II} & & & & \text{III} \end{array}$$

For structure I we get

$$\psi_{\rm I}=\tfrac{1}{2}[a(1)\beta(1)b(2)\alpha(2)-b(1)\alpha(1)a(2)\beta(2) -a(1)\alpha(1)b(2)\beta(2)+b(1)\beta(1)a(2)\alpha(2)],$$

and for structures II and III

$$\psi_{\rm II}=2^{-\frac{1}{2}}[a(1)\beta(1)a(2)\alpha(2)-a(1)\alpha(2)a(2)\beta(2)],$$

and

$$\psi_{\rm III}=2^{-\frac{1}{2}}[b(1)\beta(1)b(2)\alpha(2)-b(1)\alpha(1)b(2)\beta(2)],$$

where a and b are suitable atomic orbital functions depending upon position coordinates, and 1, 2 represent the position and spin coordinates for electrons 1 and 2. The approximate hamiltonian is supposed to be of the form,

$$H=-\frac{h^2}{8\pi^2 m}(\nabla_1^2+\nabla_2^2) +e^2\left(-\frac{Z_A}{r_{A1}}-\frac{Z_B}{r_{B1}}-\frac{Z_A}{r_{A2}}-\frac{Z_B}{r_{B2}}+\frac{1}{r_{12}}+\frac{Z_AZ_B}{r_{AB}}\right).$$

We seek

$$H_{\rm II}=\int\int\psi_{\rm I}H\psi_{\rm I}d\tau_1d\tau_2.$$

Since H does not involve spin or magnetic interactions, the integrals vanish unless all the spins match; and if all the spins match, the integrals over the spin functions are equal to unity, and we obtain

$$H_{\rm II}=\frac{1}{2}\int\int a(1)b(2)Ha(1)b(2)d\tau_1d\tau_2 +\frac{1}{2}\int\int a(1)b(2)Ha(2)b(1)d\tau_1d\tau_2 +\frac{1}{2}\int\int a(2)b(1)Ha(1)b(2)d\tau_1d\tau_2 +\frac{1}{2}\int\int a(2)b(1)Ha(2)b(1)d\tau_1d\tau_2=Q+\alpha.$$

In the same way we have $H_{\rm I\ II}=H_{\rm I\ III}=2^{\frac{1}{2}}\gamma$; $H_{\rm II\ II}=H_{\rm III\ III}=Q'$; $H_{\rm II\ III}=\alpha$; $\Delta_{\rm I\ I}=1$; $\Delta_{\rm II\ II}=\Delta_{\rm III\ III}=1$; $\Delta_{\rm I\ II}=\Delta_{\rm II\ III}=\Delta_{\rm I\ III}=0$. With these values we can set up the secular equation $|H_{XY}-\Delta_{XY}W|=0$.

For more complicated problems it is difficult to write out the functions in full in this way, and it is desirable to find a simpler notation which will serve the same purpose. The following slight modification of Pauling's arrow diagrams is convenient. For any valence bond structure, such as IV,

$$A\quad B\text{—}C\quad D\text{:}\quad \text{IV},$$

the initial disposition of the spin-orbit functions is indicated, respectively, for electrons 1, 2, 3, etc., by a row of letters, such as IVa, with both bonded and unshared pairs connected by arrows,

$$b\rightarrow c\quad d\rightarrow d,\quad \text{IVa},$$

the head of an arrow indicating initial spin function α and the tail β. The many terms of a matrix element of **H** or of unity which need to be counted can now be visualized by juxtaposing these symbols for the two structures involved, for example,

$$\frac{b\rightarrow c\quad d\rightarrow d}{b\rightarrow c\quad d\rightarrow d}\quad\text{for}\quad H_{\rm IV\ IV},$$

and imagining the spin-orbit functions to be permuted among the electrons and the arrows to be reversed, both above and below the line, in all allowed ways. (Our second prescription for the permutations and reversals, which corresponds to allowing reversal of all the arrows and ruling out permutations of identical orbitals in the symbols, turns out to be the more convenient in this connection and will be assumed in the following.) Every permutation of the spin-orbits in one of the factors can be matched by a corresponding permutation in the other so as to give rise to a number of identical contributions to the matrix element; if, therefore, we multiply by the number $(2n)!/2^{p_U}$ of allowed permutations for one of the symbols—we have arbitrarily taken the upper and designated it by the subscript U—the permutations in that symbol need not be considered further. A particular integral over the spatial coordinates, such as the integral,

$$\int b(1)c(2)d(3)d(4)Hb(1)c(2)d(3)d(4)d\tau,$$

which is directly indicated by our superposition diagram, will in general still occur a number of times, since on integrating over the spin coordinates each term which arises from the various possible reversals of arrows can only lead to the same spatial integral with a partial coefficient of ±1 or 0; furthermore, integrals which are equivalent or identical may occur a number of times corresponding to the remaining permutations, if, respectively, the molecule has symmetry or if one or more of the orbitals appears twice in the upper symbol. In any case, the coefficient of the integral which arises from a particular one of these (lower symbol) permutations is equal to the product of normalization factors,

$$2[\tfrac{1}{2}(p_U+p_L)-n]/(2n)!$$

(U and L refer to upper and lower), multiplied by $(2n)!/2^{p_U}$, and by the number of ways of matching spins, which just as in Pauling's method is 2^i, with i the number of *islands* in the juxtaposition diagram. The sign of the coefficient is given by $(-1)^{P_L+R_U+R_L}$, where P_L refers to the permutation that gives rise to the particular integral and the factor $(-1)^{R_U+R_L}$ is the same for each spin match. If we write Δp for p_L-p_U, the

coefficient may then be expressed simply as

$$2^{i-n+\Delta p/2}(-1)^{P_L+(R_U+R_L)}$$

To return to our example, the initial configuration,

$$\frac{b\to c \quad d\to d}{b\to c \quad d\to d}$$

contributes to $H_{\text{IV IV}}$ the integral Q' with coefficient $2^{2-2+0}\cdot(-1)^0=1$. The only permutations which lead to further important integrals are the exchange of b and c,

$$\frac{b\to c \quad d\to d}{c\leftarrow b \quad d\to d},$$

and of c with both d's,

$$\frac{b\to c \quad d\to d}{b \quad d \quad c \quad d}, \qquad \frac{b\to c \quad d\to d}{b \quad d\leftarrow d \quad c}.$$

Each resulting integral is of the class α', and the last two are identical; if, however, as we assume in the following, the two nonidentical integrals have approximately the same value, this contribution to $H_{\text{IV IV}}$ is

$$[2^{2+2-2+0}(-1)^{1+1}+2^{1-2+0}(-1)^{1+2}+2^{1-2+0}(-1)^{1+0}]\alpha' = (1-\tfrac{1}{2}-\tfrac{1}{2})\alpha'=0.$$

It will be noted that insofar as the desired integrals can be obtained without exchange of orbitals in the lower symbol or with only single exchanges, the arrowheads can be dropped and Pauling's familiar coefficients $\frac{1}{2}^{n-i}$ and $f/2^{n-i}$ applied. It is only necessary to make sure of the identity of the integral in question and to include the factor $2^{\Delta p/2}$. If this factor is maximized by choosing for the lower symbol the structure with the greater number of unshared pairs, the number of occurrences of identical integrals which have to be explicitly considered is, of course, minimized.

SPECIAL RULES

This method, with its use of a diagram which emphasizes the initial assignment of a labelled orbital to each electron, is very satisfactory for finding any particular coefficient; but in practice it is tedious, and we have found it profitable to derive the following more detailed but somewhat special rules, which can be used directly with the ordinary bond diagrams. No doubt more or less similar procedures useful for other cases can readily be found.

We consider a system involving an even number of electrons, and the same number of atoms arranged in a straight chain or simple ring with at most one polar bond, which may have 0, 1, or 2 atoms between the charged atoms. Those cases for the ionic structures we call ortho-, meta-, and para-, respectively.

The application of each rule is illustrated by an example taken from the benzene problem, which we have chosen for this purpose because of its general interest. It is assumed that the different integrals of each of our classes α, γ, γ', and α' are equal.

In consequence of our previous assumption that all other exchange integrals are negligible, the matrix element H_{XY} will vanish if an electron must jump to a nonadjacent atom or more than two electrons must jump to adjacent atoms in order to transform structure X into structure Y.

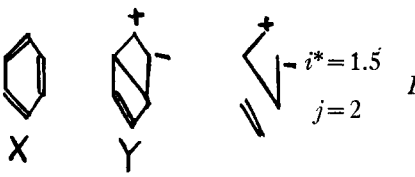
(I) $\dfrac{\text{non-ionic}}{\text{ionic}}$

(A) $\dfrac{\text{non-ionic}}{\text{ortho-ionic}}$ $\quad H_{XY}=\gamma 2^{i^*-j}.$

j = number of covalent bonds in ionic structure,

i^* = number of islands, with an open polygon counted as $\frac{1}{2}$ an island.

Example:



$i^*=1.5$, $j=2$ $\quad H_{XY}=\gamma 2^{-\frac{1}{2}}=\gamma/\sqrt{2}.$

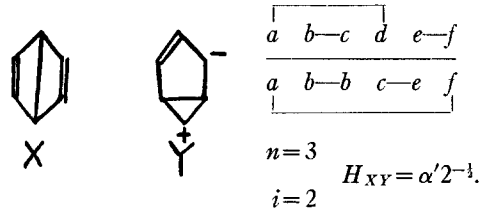
(B) $\dfrac{\text{non-ionic}}{\text{meta-ionic}}.$

For this case we have been unable to find a simple rule which is applicable to superpositions of ordinary bond diagrams, so that the matrix element has to be determined by our general method, which leads to

$$H_{XY}=\alpha' 2^{\frac{1}{2}-n+i},$$

with i the number of islands in the juxtaposition symbol.

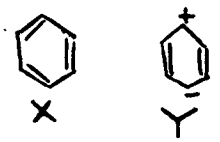
Example:



$n=3$, $i=2$ $\quad H_{XY}=\alpha' 2^{-\frac{1}{2}}.$

(C) $\dfrac{\text{non-ionic}}{\text{para-ionic}}$ $\quad H_{XY}=0.$

Example:



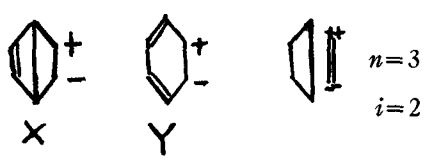
$H_{XY}=0$. (More than two electron jumps are required to change X into Y.)

(II) ortho/ortho
meta/meta
para/para

(A) Same charge distribution in both structures.

$$H_{XY}=KQ'+K'\alpha'.$$

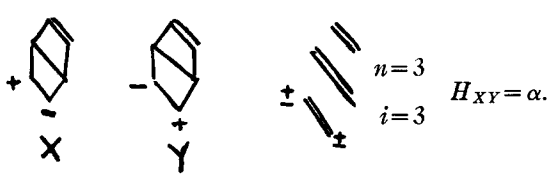
Here K and K' are calculated with Pauling's rules, as described earlier in this paper, considering an ionic bond as equivalent to a covalent bond in the determination of n and i. There are no exchange integrals with atoms positively charged, but a double number of exchange integrals with atoms negatively charged.
Example:



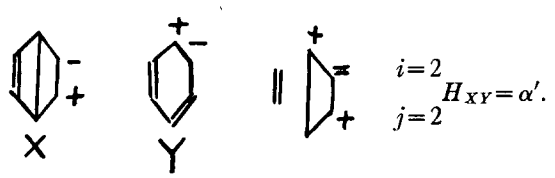
(B) Charges inverted. For ortho/ortho

$$H_{XY}=K\alpha,$$

where K is obtained in the same way as before.
Example:



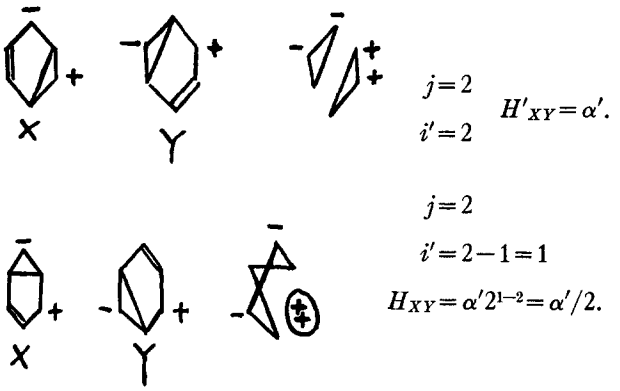
For meta/meta and para/para $H_{XY}=0$.
(C) Charges on different atoms.
(1) $H_{XY}=0$, double-jump rule.
(2) $H_{XY}\neq 0$
ortho/ortho and para/para: $H_{XY}=\alpha' 2^{i-1}$.
Example:



meta/meta: $H_{XY}=\alpha' 2^{i'-1}$.

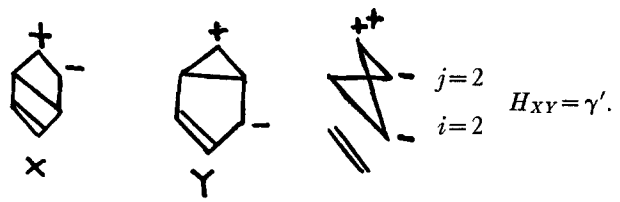
Here i' is calculated by connecting atoms with plus charge with each other, and atoms with minus charge with each other: if two negative charges fall on the same atom, the result is zero island; if two positive charges fall on the same atom, the result is one island; furthermore, if a bond between two atoms with minus charge is crossed by two covalent bonds, i' is diminished by 1; if the same thing happens to a bond between two positively charged atoms, i' is increased by 1.

Examples:



(III) ortho/meta
meta/para

(1) $H_{XY}=0$, double-jump rule.
(2) $H_{XY}=\gamma' 2^{i-1}$, otherwise.
Example:



(IV) ortho/para

(1) $H_{XY}=0$, double-jump rule.
(2) $H_{XY}=\alpha' 2^{i''-1}$, otherwise.
Here the number i'' is calculated by connecting plus with plus and minus with minus and counting islands. The group minus minus counts as zero island and group plus plus as one island.
Example:

The above rules have been applied to the treatment of some molecules with the assumption of reasonable values for Q, the several Q', α, α', γ, and γ'. The results are to be published soon.

ACKNOWLEDGMENTS

This problem was suggested to us by Professor Pauling, to whom we are also much indebted for many helpful discussions. One of us (M.S.) wishes to express thanks to the Italian Research Council for a grant.